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METHOD FOR MANUFACTURING A CLAY-POLYAMIDE COMPOSITE

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Claim

A method for manufacturing a clay-polyamide composite characterized by carrying out the polymerization of lactam in the presence of a clay-organic compound composite made by carrying out ion exchange to bond an organic compound which contains at least one amino group and has the catalyst effect of polymerizing the lactam and clay.

Detailed explanation of the invention

The present invention concerns method for manufacturing a clay-polyamide composite made with clay firmly bound to polyamide by carrying out polymerization of lactam with a catalyst bound to the clay surface.

A variety of conventional methods for making clay-polyamide composites have been suggested to improve the properties of the polyamide and to reduce costs. A method employing the addition of clay to polyamide has been known. However, because it was difficult to disperse the clay homogeneously, and because no bonding occurred between the clay and polyamide, the conventional clay polyamide composite had extremely poor strength. In order to solve this problem, a method employing surface treatment of clay with an organic compound such as an organic amine to improve the

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compatibility of the polyamide so that the properties could be improved has been suggested. However, clay cannot be firmly bound to polyamide.

The objective of the present invention is to provide a method for manufacturing a clay-polyamide composite made by firmly bonding the clay to the polyamide to improve the extremely poor strength of the conventional clay-polyamide composite.

The objective was completed by the following present invention. The present invention involves a method for manufacturing a clay-polyamide composite characterized by carrying out the polymerization of lactam in the presence of a clay-organic compound composite made by carrying out ion exchange to bond an organic compound which contains at least one amino group and has the catalyst effect of polymerizing the lactam and clay.

Examples of the organic compound used in the present invention and containing at least one amino group and having the catalyst effect of polymerizing the lactam, include the following: ω-aminocapronic acid; a nylon salt; hexamethylenediamine; aminoundecanoic acid.

The lactam used for the present invention is not specifically restricted to ε-caprolactam. A lactam with a carbon number of 7-12 such as ω-enantolactam, ω-capryllactam, or ω-laurolactam can be used.

Examples of the clay used in the present invention include the following: montmorillonite group clay minerals such as montmorillonite, hectorite, nontronite, or saponite; vermiculite group clay minerals such as vermiculite; kaolin group clay minerals such as kaolin; multiple-chain lattice clay minerals such as attapulgite. Because the capacity of bonding an organic

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compound having the catalyst effect of polymerizing clay is equal to the capacity of exchanging clay with a base, the following having a large capacity of exchanging with a base: montmorillonite; hectorite; nontronite; saponite; vermiculite are especially suitable. In both cases of montmorillonite group clay minerals and vermiculite clay minerals which have the three-layer crystal structure of clay, and when an exchangeable cation present in the crystal layers of the clay is exchanged with sodium, ion exchange with the organic compound having the polymerization catalyst effect can be quickly carried out, so that the objective can be easily completed.

The composite can be made by ion-exchanging clay with an organic compound having the catalyst effect, which is influenced by the type of organic compound used or by the concentration, temperature, or pH of the solution. The solution of organic compound at 50°C, with a 0.1-1M concentration, and with an acidic pH is suitable. After the reaction, the clay suspension obtained in the reaction is filtered, repeatedly washed with water, dried, then crushed to make a clay-organic compound composite.

The temperature for carrying out the polymerization of lactam in the presence of the clay-organic compound composite is not specifically restricted. However, a temperature of 240-260°C known by experts, is suitable. The amount of the clay organic compound composite added is not specifically restricted. However, an addition amount of the clay organic composite of 10-75 wt% of the lactam is suitable. When the amount is less than 10 wt%, the amount of nonreacted lactam increases. When the amount is more than 75 wt%, a clay-polyamide composite which is able to form good molded products cannot be made.

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The present invention effectively carries out the polymerization of lactam with a catalyst bound to the clay surface to firmly bond the clay to the polyamide to form a clay-polyamide composite.

Because the clay is firmly bound to the polyamide and because a large amount of clay is contained when the clay-polyamide composite is made by a method of the present invention, the composite can be molded to produce fire-retardant molded products, or the composite can be added to a polymer to produce products that can be used as reinforcing materials for polymers.

The fire-retardant effect of the clay-polyamide composite made by the method of the present invention is different from that obtained by using a fire retardant. Toxic gas is not produced from a fire retardant during combustion, and the heat value can be reduced. It can be used to improve the fluidity of coating materials, printing inks, or lubricating grease. It can be used for an adsorbent because polyamide has adsorbability.

In the following, the details of the present invention are explained with both application and comparative examples.

Application Example 1

10 g montmorillonite were immersed in 150 mL of a 1M aminocapronic acid aqueous solution with a pH of 5.2 obtained by adjustment with sulfuric acid to carry out ion exchange at 65°C for 24 h. The produced clay suspension was filtered, repeatedly washed with water, dried, then crushed to make a montmorillonite-aminocapronic acid composite having a particle size of 100 mesh or less (149 µm or less).

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The produced composite was vacuum dried at 80°C for 1 h, then both 9 g of the dried sample and 20 g caprolactam anhydride were introduced into a previously substituted polymerization tube, then degassing was performed under reduced pressure, then nitrogen was introduced to completely remove air from the polymerization tube. Then, lactam was melted at 80-100°C in the nitrogen flow to stir and mix the sample, then the temperature was increased to obtain a minimal nitrogen flow, then polymerization of lactam was performed at 250°C for 6 h. After the polymerization was complete, the produced product was crushed to obtain a particle size of 100 mesh for the product. Then, extraction was performed using hot water while stirring for 24 h to remove nonreacted products. A montmorillonite-polyamide composite was made.

The content of polyamide in the montmorillonite-polyamide composite was determined by extracting the composite with formic acid after extraction using hot water, then calculating both the amount of extracted polymer and the amount of remaining polymer (not extracted). Polyamide was contained in the produced montmorillonite-polyamide composite at 37 wt%. The distance between the montmorillonite crystal layers was given by subtracting 9.6 Å of a silicate layer from the distance between the surfaces (001) measured by X-ray diffraction. While a distance of 3.4 Å between the montmorillonite and aminocapronic acid composite layers was obtained before polymerization was carried out, and a distance of 13.1 Å was obtained after polymerization was carried out. The increase in the distance between the layers indicated that polymerization was carried out between the crystal layers.

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Application Example 2

A montmorillonite-nylon chloride composite was made using the same process in Application Example 1 except for using nylon chloride instead of aminocapronic acid. The polymerization of caprolactam anhydride was carried out in the presence of the composite using the same process in Application Example 1 except for using both 7.5 g of dry montmorillonite-nylon chloride composite and 15 g of caprolactam. After the polymerization was complete, the same treatment used in Application Example 1 was performed.

Polyamide was contained in the montmorillonite-polyamide composite at the amount of 14 wt%. A distance of 6.2 Å between the layers of the composite was obtained. A distance of 3.4 Å between the layers of the montmorillonite-nylon chloride composite used for polymerization was obtained.

Application Example 3

A montmorillonite-aminocapronic acid composite made using the same process in Application Example 1 was crushed, a 325-mesh particle size of the composite (44 μm) was obtained by adjustment, then polymerization was carried out using the same process in Application Example 1 in the presence of the composite. After polymerization was complete, a montmorillonite-polyamide composite was made using the same process in Application Example 1.

After extraction using hot water was performed, the above-mentioned composite having 100 mesh or less was again crushed to obtain a particle size of 325 mesh or less.

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Application Example 4

10 g montmorillonite were immersed in 150 mL of a 1M aminoundecanoic acid hydrochloride aqueous solution with a pH of 2.0 obtained by adjustment with sulfuric acid to carry out ion exchange at 65°C for 24 h. The produced clay suspension was filtered, repeatedly washed with mixed solution of water with methanol (water:methanol = 1:2), dried, then crushed to make a montmorillonite-aminoundecanoic acid composite having a particle size of 100 mesh or less.

A montmorillonite-polyamide composite was made using the same process in Application Example 1 except for using both 10 g of the montmorillonite and aminoundecanoic acid composite and 41.8 g of caprolactam anhydride.

Polyamide was contained in the montmorillonite-polyamide composite at an amount of 66.8 wt%. A distance of 6.5 Å between the montmorillonite-aminoundecanoic acid composite layers was obtained before polymerization was carried out. A distance of 50.6 Å between the montmorillonite-polyamide composite layers was obtained after polymerization was complete.

Comparative Example 1

The polymerization of caprolactam anhydride was carried out in the presence of 8 g montmorillonite vacuum-dried at 80°C for 4 h using the same method in Application Example 1. The same treatment performed in Application Example 1 was performed after polymerization was complete. Polyamide was contained in the sample in the amount of 0.0% after extraction with hot water.

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Each montomorillonite-polyamide composite made in Application Examples 1-4 was molded, then the properties of each product were measured. Each montomorillonite-polyamide composite made in Application Examples 1-4 and a nylon 67 chip having a relative viscosity of 3.4 were separately vacuum-dried at 80°C for 4 h, homogeneously mixed together at 270°C in a nitrogen flow, then extruded from a nozzle (diameter: 1.0 mm) using an [illegible] type flow tester. A product (diameter: 0.6 mm) was made. Each montmorillonite-polyamide composite made in Application Examples 1-4 was molded under the same conditions. Both nylon 6 and nylon 6 with added montmorillonite were separately molded under the same conditions.

An elongation test was performed for each molded product. The results are shown in Table 1. Measurement was performed using each product which was wet at 24°C at 60% RH for 48 h at an elongation rate of 100%/min.

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Table 1

	10	11	12	13	14
1 成形品	粘土ポリアミド複合体含有量(重量部)	ポリアミド含有量(重量%)	引張強度 (kg/cm²)	ヤング率 (kg/cm²)	伸度 (%)
2 (比較例)ナイロン6	-	100	1.05×10^3	0.81×10^4	556
3 (比較例) モンモリロナイト添加ナイロン6	-	70	0.23×10^3	2.35×10^4	4
3 (比較例) モンモリロナイト添加ナイロン6	-	50	0.09×10^3	1.39×10^4	1
4 実施例1のモンモリロナイト-ポリアミド複合体	100	37	0.31×10^3	2.67×10^4	2
5 実施例1のモンモリロナイト-ポリアミド複合体添加ナイロン6	50	81	0.45×10^3	1.97×10^4	212
6 実施例2のモンモリロナイト-ポリアミド複合体添加ナイロン6	30	74	0.38×10^3	1.91×10^4	12
7 実施例3のモンモリロナイト-ポリアミド複合体添加ナイロン6	60	81	0.81×10^3	2.67×10^4	331
8 実施例4のモンモリロナイト-ポリアミド複合体	100	67	0.36×10^3	3.62×10^4	1
9 実施例4のモンモリロナイト-ポリアミド複合体添加ナイロン6	60	90	0.58×10^3	2.63×10^4	2

Key:
1 Molded product
2 (Comparative example) Nylon 6
3 (Comparative example) Nylon 6 with added montmorillonite
4 Montmorillonite-polyamide composite made in Application Example 1
5 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 1
6 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 2
7 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 3
8 Montmorillonite-polyamide composite made in Application Example 4

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9 Nylon 6 with montmorillonite-polyamide composite made in Application Example 4
10 Content of clay-polyamide composite (wt%)
11 Content of polyamide (wt%)
12 Tensile strength (kg/cm^2)
13 Young's modulus % (kg/cm^2)
14 Elongation (%)

The montmorillonite-polyamide composites made in Application Examples 1-4 could be molded by themselves. As seen in Table 1, molded products made with montmorillonite-polyamide composites made in both Application Examples 3 and 4 had a lower tensile strength than that of a product made with nylon 6, but both had a larger strength and a larger Young's modulus percentage than those of a product made with nylon 6 with added montmorillonite. Therefore, it was verified that the properties could be improved by using the composite. Molded products made with nylon 6 and the montmorillonite-polyamide composite made in Application Example 1 and made with nylon 6 and the montmorillonite-polyamide composite made in Application Example 2 had a larger tensile strength than that of a product made with added montmorillonite.

Both the water absorbency and dimensional stability of each molded product were measured. Table 2 shows the results. Measurement was performed by immersing each product having a length of 30 cm and vacuum-dried for 1 day at 120°C in water at 20°C for 24 h.

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Table 2

	9	10	11	12
1 成形品	粘土-ポリアミド複合体含有量(重量%)	ポリアミド含有量(重量%)	吸水率(%)	寸法変化(%)
2 (比較例)ナイロン6	-	100	10.1	2.9
3 (比較例) モンモリロナイト添加ナイロン6	-	70	10.2	3.2
3 (比較例) モンモリロナイト添加ナイロン6	-	50	12.5	4.4
4 実施例1のモンモリロナイト-ポリアミド複合体	100	37	4.1	0.0
5 実施例1のモンモリロナイト-ポリアミド複合体添加ナイロン6	50	61	6.7	1.1
6 実施例2のモンモリロナイト-ポリアミド複合体添加ナイロン6	50	74	4.4	1.0
7 [illegible] 複合体	100	67	1.4	4.1
8 実施例4のモンモリロナイト-ポリアミド複合体添加ナイロン6	50	90	6.1	0.5

Key:
1 Molded product
2 (Comparative example) Nylon 6
3 (Comparative example) Nylon 6 with added montmorillonite
4 Montmorillonite-polyamide composite made in Application Example 1
5 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 1
6 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 2
7 Montmorillonite-polyamide composite made in Application Example 4
8 Nylon 6 with added montmorillonite-polyamide composite made in Application Example 4
9 Content of clay-polyamide composite (wt%)
10 Content of polyamide (wt%)
11 Water absorbency (%)
12 Dimensional stability (%)

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The dimensional stability of molded products made with nylon 6 with a montmorillonite-polyamide composite made in either Application Example 1 or 2 was significantly improved. A molded product made with the montmorillonite-polyamide composite of Application Example 1 had no dimensional stability and extremely poor water absorbency.

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